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ABSTRACT

The work of Noid *et al*. [J. Chem. Phys., **67**, 404 (1977)] has shown that sharp molecular spectra can be obtained through a Fourier transform of the autocorrelation function of a classical trajectory. In the present work, we extend this idea to obtain a spectrum by Fourier transform of the dipole moment function of collision product trajectories. We show that this "classical collision spectrum" (CCS) is related to the cross section for creating the product times an Einstein A factor. As a test case, we analyze product CO trajectories obtained from O + CO collisions at 8 km/sec and focus on the spectral resolution of the CCS. The CCS of these trajectories shows rich quantum-like features, including well-separated vibrational overtones and rotational band-heads, which become more pronounced with particular trajectory weighting methods. For polyatomic cases, the hope is that the CCS can be deconvolved into ro-vibrational specific probabilities and cross sections, which would otherwise overlap in a conventional classical trajectory energy analysis.

I. INTRODUCTION

About thirty years ago, Noid *et al.* demonstrated how molecular spectra could be obtained from analysis of classical trajectories.[1] By Fourier transforming a suitable autocorrelation function, accurate, sharp-featured spectra were obtained for several model Hamiltonian systems. More recently, Fourier analysis of the velocity autocorrelation and dipole moment functions of classical trajectories have been used to analyze the dynamics and generate spectra for a wide variety of systems, including CH_5^+ (Ref. 2) and the hydrated proton.[3] In the present work, we extend the work of Noid *et al.* to an analysis of spectra of quasi-classical trajectory (QCT) collision products. The goal is to develop improved methods of characterizing the final state collision products in terms of quantum-specific states. For polyatomic products, conventional QCT binning methods have great difficulty in separating ro-vibrational cross section contributions due to overlaps in a particular energy bin. Although methods have been developed to generate classical ro-vibrational specific cross sections,[4] these methods have proven difficult to apply to general cases.

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The calculation procedure we developed involves first performing QCT calculations of molecular collisions at a particular collision energy, with each trajectory sampling a range of orientation and impact parameters in the usual way.[5] At the end of each trajectory, however, we retain the final positions and momenta of the collided products. Then, using this set of final positions and momenta, we continue each trajectory and Fourier transform the dipole moment of the collided products. The weighted average of these transforms is a "classical collision spectrum" (CCS) of the nascent collision products, which is related to the cross section for creating the product times an Einstein A factor.

The CCS, obtained by straightforward extension of standard QCT methods, may offer several benefits for analysis of classical trajectories. With knowledge of measured or calculated product Einstein A values, and if final product spectral contributions do not overlap too much, it may be possible to deconvolve the CCS and estimate quantum specific cross sections. The idea is that ro-vibrational product cross sections, which would otherwise overlap in a conventional internal energy analysis, will separate more cleanly in the classical collision spectrum. The CCS may also be compared directly to molecular beam experiments where spectra of the nascent collision products are measured, providing a useful common point of analysis between experimental observables and theory. Finally, as ab-initio molecular dynamics becomes more routinely used, with accurate forces and dipole moments available at each trajectory step, generation of the CCS should be readily achievable, even for very large molecules.

In Section II, we develop the theory of the CCS. Starting with the work of Noid *et al.*, we obtain an expression relating the CCS of a single trajectory to a set of Einstein A values and transition energies. We then show that the weighted average of classical spectra can be related to the ro-vibrational specific cross section times a set of Einstein A values. In Section III, we illustrate the method by examining $O(^3P)$ + $CO(^1\Sigma_g)$ collisions at 8 km/sec. We used the potential energy surfaces and product CO trajectories of our previous QCT studies,[6,7] in which the product state distributions compared well to measurements.[7-9] For the CO diatomic product, conventional QCT methods provide ro-vibrational specific cross sections which serve as a benchmark test case with which to compare the CCS results. We first investigate the dependence of the CCS results on the semi-classical vibrational and rotational actions and on numerical integration errors for single CO(v,j) semi-classical trajectories. We then generate classical spectra of the product CO, averaging over a large set of O + CO trajectories. The resulting CCS of the O + CO collision trajectories shows rich quantum-like features, including well-separated vibrational overtones and rotational band-heads, which become more pronounced with particular trajectory weighting methods. In Section IV, we give conclusions and discuss possible future applications to polyatomic systems.

II. METHODS

In this section we derive an expression relating the Fourier transform of the dipole moment of a single classical trajectory to a set of Einstein A values and transition energies, which we call a classical collision spectrum (CCS). We then show that a weighted average of these CCS is related to the product of a ro-vibrational specific collision cross section times this set of Einstein A values. In principle, these relationships allow the deconvolution of the averaged CCS obtained from trajectories of collision products into ro-vibrational specific cross sections.

Following Noid *et al.*,[1] we start with the definition of the line-shape function, *I(w)*:

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} C(t) e^{-i\omega t} dt, \tag{1}$$

where *C(t)* = <*x(0)x(t)*> is the autocorrelation of the some dynamical variable, *x(t)* (coordinate, dipole moment, etc.), and the brackets denote an ensemble average. Noid *et al.* show that for an ergodic or quasi-periodic trajectory, the brackets can be removed to yield an expression,

$$I(\omega) = \frac{1}{2\pi} \lim_{T\to\infty} \frac{1}{T} \left| \int_0^T x(t) e^{-i\omega t} dt \right|^2 . \tag{2}$$

For an absorption line shape, the dynamical variable $x(t) = \vec{\mu}(t)$, where $\vec{\mu}(t)$ is the dipole moment function. We can relate the absorption line shape, $I(\omega)$, to the absorption cross section, $\alpha(\omega)$, of a single trajectory,[10]

$$\alpha(\omega) = \frac{4\pi\omega\, I(\omega)}{3\hbar c} . \tag{3}$$

The integral of the absorption cross section with respect to the frequency near an absorption line center, is the absorption coefficient, S, which is related to the Einstein A value,[11]

$$S = \int \alpha(\omega) d\nu = \frac{c^2}{8\pi^2 \nu^2} A_{ul} \frac{g_u}{g_l}. \tag{4}$$

In the above equation, A_{ul} is the Einstein A coefficient from an upper state, *u*, to a lower state, *l*, and g_u and g_l, respectively, are the degeneracies of the upper and lower states. We note that the full absorption spectrum will contain a number of lines connecting the lower state *l* to a set of upper states *{u}*. Substituting Eq. (3) into Eq. (4), and using Eq. (2) for the absorption line shape, we can relate the Einstein A coefficients to the Fourier transform of the dipole moment function of a single trajectory:

$$A_{\{u\}l}(\lambda) = \frac{64\pi^4}{3h\lambda^3}\frac{g_l}{g_u}\int d\nu \frac{1}{T}\left|\int_0^\infty \vec{\mu}(t)e^{-i\omega t}dt\right|^2 . \tag{5}$$

In Eq. 5, λ is the wavelength, and $A_{\{u\}l}(\lambda)$, which we call the classical collision spectrum (CCS), is a set of Einstein A coefficients connecting the lower state *l* with all dipole allowed upper states *{u}* at the transition wavelengths $\lambda_{l\{u\}}$ = {λ_{lu1}, λ_{lu2}, etc.}. In other words, the expression $A_{\{u\}l}(\lambda)$ represents a classical analog of an absorption stick spectrum of a particular ro-vibrational state *l* defined by the initial position and momentum of the trajectory. The peak heights are directly proportional to the Einstein A values from the upper state *u* to the lower state *l*, and the wavelengths at which the peaks appear are the transition wavelengths from *l* to *u*. Formulating the CCS in this way facilitates comparison to literature values of the Einstein A coefficients. To evaluate Eq. (5) in practice, we compute a discrete Fourier transform over a time window of length *T* for each of the vector components of the dipole moment function, and we approximate the integration interval over the frequency, ν, around each line by multiplying each Fourier transform frequency bin by the bin width, $\frac{1}{T}$,

$$A_{\{u\}l}(\lambda_k) \approx \frac{64\pi^4}{3h\lambda^3}\frac{g_l}{g_u}\frac{1}{T^2}\left[\left|\Delta t\sum_{n=1}^{N}\hat{x}\cdot\vec{\mu}(t_n)e^{-i2\pi nk/N}\right|^2 + \left|\Delta t\sum_{n=1}^{N}\hat{y}\cdot\vec{\mu}(t_n)e^{-i2\pi nk/N}\right|^2 + \left|\Delta t\sum_{n=1}^{N}\hat{z}\cdot\vec{\mu}(t_n)e^{-i2\pi nk/N}\right|^2\right]$$

(6).

In equation 6, Δt is the discrete Fourier transform time step, $T = N\Delta t$, where *N* is the number of Fourier transform time steps, $\{\hat{x}, \hat{y}, \hat{z}\}$ are unit vectors along the Cartesian $\{x, y, z\}$ directions, *n* denotes a time bin, and *k* a frequency bin.

Now suppose a number of molecular trajectory collisions are performed in the standard QCT manner, where an average over the relative orientation of the reagents and over the collision impact parameter is taken in the usual way. For a particular trajectory, once the products are far away from each other, we take the position and momentum of one of the products to define the ro-vibrational state *l*. Analogous to the expression for the collision cross section, we write the average of the CCS over a number of such trajectories,

$$\overline{A}(\lambda) = \frac{1}{\sum_{l}^{N_{tot}} w_l} \sum_{l}^{N_{tot}} w_l \, A_{\{u\}l} \, . \tag{7}$$

In Eq. (7), N_{tot} is the total number of trajectories, w_l is the weight of the trajectory with final position and momentum *l*, and $A_{\{u\}l}$ are CCS of individual trajectories associated with a particular *l*. Using standard QCT methods for choosing the initial orientation of reagents and products and if we bin the *l* states into quantum specific ro-vibrational product states, *q*, we can write the weights in terms of probabilities and cross sections,

$$P_q = \frac{\sum_{l \to q} w_l}{\sum_{l}^{N_{tot}} w_l} = \frac{\sigma_q}{\sigma_{tot}} = \frac{\pi b_{\max}^2 \sum_{l \to q} w_l}{\pi b_{\max}^2 \sum_{l}^{N_{tot}} w_l}, \tag{8}$$

where in Eq. (8), $\sum_{l \to q} w_l$ represents the sum of all those trajectories, *l*, binned into ro-vibrational state, *q*, b_{max} is the maximum impact parameter of the QCT calculations, σ_q is the cross section to the ro-vibrational product state *q*, P_q is the probability of forming the products in state *q*, and σ_{tot} is the sum of all σ_q. We now write Eq. (7) in terms of the probability of molecular collisions which lead to the ro-vibrational state *q*,

$$\overline{A}(\lambda) = \sum_{q} P_q \, A_{\{u\}q} \, . \tag{9}$$

Equations (6-9) are the main results of this section. Eq. (9) shows that the averaged CCS, $\overline{A}(\lambda)$, can be interpreted as an absorption spectrum of the nascent products of molecular collisions. These equations also provide an alternative way to estimate the ro-vibrational specific probabilities and cross sections from standard QCT methods. We first generate the CCS average, $\overline{A}(\lambda)$, from Eqs. (6) and (7). Then with knowledge of the Einstein A coefficients we can deconvolve the spectrum for the quantum specific probabilities P_q using Equation (9). The hope is that the average CCS will separate contributions of different product states, *q*, which would otherwise overlap in conventional energy binning analysis.

The usefulness of the averaged CCS and the deconvolution procedure will depend on how cleanly the averaged CCS separate into ro-vibrational contributions and in the details of numerical implementation.

In the next section we investigate these issues by examining the CCS of single trajectories of the CO molecule and by using various weighting methods to compute averaged CCS for collisions of CO with atomic oxygen.

III. RESULTS

A. Single Trajectories

We now examine CCS of single trajectories of the CO molecule. All results use the potential and QCT methods of Refs. 6 and 7 and the CO dipole moment function of Ref. 12. Figure 1 shows four different CCS, each computed with Eq. (6). Each CCS used different initial positions and momenta, l , labeled by their semi-classical actions, (v=0,j=90), (v=1,j=90), (v=2,j=90), and (v=3,j=90), and prepared using standard WKB methods.[5] The trajectories were integrated with a standard velocity Verlet algorithm,[13] with 10^6 time steps of $1.x10^{-16}$ seconds spacing. The FFT of each trajectory was obtained by zero-padding the trajectory to the next power of 2, 2^{20} points, giving a spectral bin width of 0.318 cm^{-1}. These parameters are associated with our 'standard' numerical convergence parameters. Examining a single trajectory, we observe the expected absorption progression of Δv=0,1,2,3 peaks. The Δv=0 region contains one transition corresponding to an "absorption" from j=90→ 91. The other spectral regions each have "P" and "R" pair peaks associated with a unit change in the rotational "quantum number". As shown below, the peak positions are all within ~10 cm^{-1} of reference positions for transitions obtained by computing the WKB energies with this same potential, and the values of the Einstein A coefficients agree qualitatively with benchmark calculations using a similar quality potential and dipole moment function. It is interesting that several quantum features of the absorption spectrum, including overtones and rotational selection rules, are recovered fairly well by a such classical trajectories.

As Noid *et al.*[1] show, the exact spectral peak locations will depend on the choice of semi-classical quantum number. Figure 2 shows the CCS of CO computed with Eq. (6) near Δv=1 transitions. Five spectra are shown, each with a different classical action l=(v,j) centered around (v=1,j=90): (v=0.5,j=90), (v=0.75,j=90),(v=1.0,j=90), (v=1.25,j=90), and (v=1.5,j=90). As the classical action is varied near a vibrational action of 1.0, the peak positions shift and the peak heights change. To examine this more in depth, Figure 3 shows the transition energy versus error in CCS peak position for 11 different transitions associated with the progression, v,j=90 → v-1,j=89, where v = 1→11. We chose to analyze this progression in depth because these transitions are prominent in the band-head structure of the emission spectra of 8 km/sec O + CO collisions[6-9] and because the results are fairly representative of other transitions we have examined. The reference transition energies are obtained by computing the WKB energies of CO with the same potential with the semi-classical quantum numbers (v = 1→11,j=90) and

(v=0→10,j=89) and taking the difference between the results. The CCS results are obtained with trajectories composed of 10^7 time steps of 10^{-18} seconds in width. The Fourier transform was obtained by zero-padding the trajectory to the next power 2 making 2^{24} points, giving a spectral bin width of 0.0199 cm^{-1}. These parameters are associated with our 'fine' numerical convergence parameters. For averages over many trajectories, fine parameter convergence can become impractical, but for single trajectories they are useful to illustrate the degree of numerical error in practical computation. The error shown Figure 3 is the CCS peak energy bin value minus the corresponding WKB transition energy. CCS results are shown for 5 different choices of the semi-classical quantum number (n,r): (n=v-0.5,r=89.5), (n=v-0.5,r=90), (n=v-0.5,r=89), (n=v,r=89.5), and (n=v-1,r=89.5). These five choices show the variation in the CCS peak positions with variations of the semi-classical action over a vibrational and rotational bin. As Noid *et. al.* show, the most accurate results are obtained by choosing a semi-classical action which is mid-way between the lower and upper states involved in the transition. These transitions correspond to the progression labeled (n=v-0.5,j=89.5), and give a nearly constant error with respect to the WKB energy of about -0.5 cm^{-1}. Varying the rotational action across a rotational bin, from j=89.0 to j=90.0, the energy error reaches about +/- 4 cm^{-1}. Varying the vibrational action across a vibrational bin from n=v-1 to n=v the energy error reach about +/- 12 cm^{-1}. Investigations of several other transitions yield a similar result. Calculations with the 'standard' numerical convergence parameters give nearly the same absolute errors in peak positions. This means that for transitions to the fundamental band, Δv=1, there will be an inherent spread of the spectral peak positions of about 30 cm^{-1} with uniform (histogram) trajectory weighting, which although not very large, may wash out some of the expected structure in the collision averaged CCS of Eq. (7). Furthermore, for the first overtone band, we can expect the energy error spread to be larger, as trajectories with vibrational actions from v=0 to v=2 for example (centered around v=1), will all contribute to the v=0 → v=2 peaks.

To investigate the accuracy of the CCS peak heights, Figure 4 shows the CCS Einstein A coefficients for fundamental (Δv=1,v→v-1,v=1-9,j=90→89) and overtone (Δv=2,v→v-2,v=2-8,j=90→89) progressions in CO as a function of the vibrational action. Results from three different CCS calculations are shown: the rotational action j=89.5 with fine numerical convergence, j=90.0 with fine numerical convergence, and j=89.5 with standard numerical convergence. We also show the computed Einstein A results of Chandra *et al.*[14] obtained with a different, but comparable CO potential and dipole moment function for a point of comparison. The Chandra *et al.* results are plotted at the average quantum number of the transition involved, (v+(v-1))/2 for the fundamental and (v+(v-2))/2 for the overtone, to more clearly illustrate the trends. It is well-known that Einstein A values, especially for higher vibrational states, are highly dependent on the fine details of the potential and dipole moment function. However, the Chandra *et al.* results will be a useful guide to the basic accuracy of the CCS peak heights and will

indicate the degree accuracy expected of the CCS when highly accurate but not 'exact' potentials and dipole moment functions are used. Except for the largest vibrational levels, the CCS fine integration results with j=89.5 agree qualitatively with the results of Chandra *et al.* when the vibrational actions are equal to the average values of the transitions. This agrees with the work of Noid *et al.* and is consistent with the analysis of the energy values in Figures 2 and 3. Values of the Einstein A coefficients change smoothly with vibrational action. The relative change in the Einstein A values with vibrational action bracketing a particular transition, however, is much larger than the corresponding energy values. For example, for the fundamental transitions, the CCS Einstein A values change by a factor of ~4 going from a vibrational action of 0 to 1, with the value at vibrational action of ½ agreeing best with the Chandra *et al.* value. There is a much smaller sensitivity of the Einstein A to the rotational action. The integration error going from standard to fine convergence is surprisingly large for the fundamental band, especially for higher vibrational levels. For the overtone progression, we observe all the same trends, except that the differences between the Chandra *et al.* and CCS results are much less, and the integration errors are far less. The good agreement is probably due to a cancellation of errors.

B. Averaged trajectories

We now present results for the averaged CCS, Eq. (7). We will examine the collision system O + CO at 8 km/sec and use the product CO position and momenta from previous QCT calculations.[6,7] A large spread of product CO vibrational and rotational states are accessed (v=10+ and j=100+), so this collision system makes for a good test case. Figure 5 shows averaged CCS calculated with 'standard' integration parameters over a large scale, with a weight of one for each trajectory. The spectrum labeled "Reference" is used for comparison. This "Reference" spectrum is computed from Eq. 9, where the probabilities P_l are obtained from standard histogram binning into CO(v,j) states, the Einstein $A_{\{u\}l}$ are taken from Chandra *et al.*,[14] and the peak positions are taken from the WKB energies of individual (v,j) lines. The averaged CCS results have been divided by the energy bin width of 0.318 cm^{-1} and the Eq. 9 reference spectral peaks have been summed into 2.5 cm^{-1} bins to give common units of (1/(seconds cm^{-1})) to facilitate comparisons. We also note that both the averaged CCS results and the reference spectrum contain contributions from each of the three lowest triplet electronic states involved in the O + CO collision system. For the averaged CCS, 1.e5 trajectories were averaged over for each electronic state, while the reference spectrum contained 2.5e5 trajectories to compute the QCT probabilities. In both spectra, most of the spectral intensity is due to "absorption" spectra of CO(v=0,j) product states (vibrationally elastic collisions), but the higher CO vibrational states also contribute significantly. The averaged CCS reproduces the overall intensities and extent of the different vibrational bands semi-quantitatively. We do not expect exact agreement, as the Einstein A coefficients of the reference spectrum were obtained with a

different potential and dipole moment function. However, there are some systematic differences which are due to the nature of the CCS. The averaged CCS is missing the band head structure due to high rotational state transitions evident in the Δv=2 and Δv=3 part of the reference spectrum. This is due to the spread of vibrational and rotational actions in each band, which shifts the position and modulates the strength of the CCS spectral lines. The shift and modulation of individual spectral lines tends to wash out any structure within a band. We have noted that as more trajectories contribute to the averaged CCS, the very fine structure evident in the Δv=4 manifold tends to wash out, as in the Δv=1 band. The averaged CCS also contains structure extending past the high energy part of the reference spectrum in each Δv region. This is due to the contributions from the large number of collisions which end up with vibrational actions near and below 0 (vibrationally elastic collisions). For these collisions the transition energies will tend to be over-estimated, and this will give a spurious blue edged contribution to each Δv progression. We also note that as the number of averaged trajectories becomes greater and the sampling of vibrational and rotational actions becomes more continuous, the fine structure in each Δv progression begins to smooth away. This is due to modulation of peak positions and peak heights with the vibrational and rotational action of each single CCS trajectory contributing to the average.

We now investigate how choices of trajectory weights can bring out interesting structure in the averaged CCS and diminish some of the differences with the reference spectrum. We introduce a Gaussian weighting function of the form,[15]

$$G(v,s) = \frac{\beta}{\sqrt{\pi}} \exp(-(\beta(\mathrm{mod}(v+s,1.0)))^2), \tag{10}$$

where v is the vibrational action. In Eq. (10), s can take on two values: either 1.0 which more heavily weights vibrational actions near integer values (G1 weighting), or 1.5 which more heavily weights half integer values of the vibrational action (G1/2 weighting). The value of β is the bin-width parameter. Following previous experience,[15] we used a value of β=16.651 which corresponds to a full-width-half-maximum (FWHM) of 0.1 across a vibrational action bin-width of 1.0. Figure 6 shows a close-up of the Δv=1 fundamental region of the averaged CCS spectra using various trajectory weights. We also show the reference spectra where we have removed the vibrationally elastic (v=0) contributions to the sum of Eq. 9 and instead of P_l we use P_u so the most blue transition (l → u) is 0→1, rather than v=1→ 2. Removing the dominant v=0 contributions and plotting the reference spectrum in this way brings out the band head structure of the very high CO rotational states excited in the collision, which are labeled by their upper vibrational state. There are three average CCS results using different kinds of weights. Figure 6a shows the results including all vibrational actions greater than v=0.5 and with weights of 1.0 for each trajectory,

which we call histogram binning (H). Figure 6b shows the averaged CCS using Gaussian half integer (G1/2) binning, according to Eq. 10, where only trajectories with vibrational actions greater than v=0.0 are kept. Figure 6c shows Gaussian integer binning (G1), where only trajectories with vibrational actions greater than v = 0.5 are kept. The histogram binned results recover the extent, general shape, and magnitude of the reference spectra well. However, the histogram binned results wash out the band head peaks. This is due to the modulation of the peak height and position with the vibrational and rotational action which are equally weighted across bins. For the Gaussian half integer weighted results, the band head structure is recovered well. For the fundamental band, the half-integer action weighting reduces the range of the vibrational action to regions near the half integer values, which are optimal for the $\Delta v=1$ fundamental band. The Gaussian integer weighted results recover the band-hand structure, but they are shifted too low in energy. The lowest vibrational actions (highest energy fundamental transitions) for the Gaussian integer results are centered near v=1, which is optimal for $v=1\rightarrow 2$ and shifted too low in energy for the $0 \rightarrow 1$ reference peak.

Figure 7(a-c) shows the same reference spectrum and average CCS results, but in the spectral range of the first overtone, $\Delta v=2$. As in the previous figure, the (a)-(c) results show histogram, Gaussian half, and Gaussian integer weighting respectively. For the first overtone region, the Gaussian integer weighted results have the best match to the reference spectrum, reproducing the band head structure of the reference spectrum in detail. For the overtone reference spectra, the highest energy transitions are $0 \rightarrow 2$, and the averaged CCS centered on integer vibrational actions of 1 and higher, as is the Gaussian integer results, are optimal. Figure 8(a-c) shows the same reference and weighted results, but in the second overtone region, $\Delta v=3$. Here the half-integer weighted results appear to match the reference spectra best. However, we note that at the high energy end of the spectrum, the average CCS extends past the reference spectrum. This is because the highest energy band-head corresponds to $0\rightarrow 3$ transitions, which corresponds to an optimal vibrational action of 1.5. Our half-integer Gaussian weighted average, however, starts with a vibrational actions centered around 0.5, giving transition energies that are too large.

IV. CONCLUSIONS

In this paper, we formulated an extension of the work of Noid et al.[1] to obtain classical spectra through Fourier transform of the dipole moment function of collision product trajectories. We showed that this "classical collision spectrum" (CCS) is related to a set of Einstein A values and transition energies. We then showed that a weighted average CCS, obtained in the usual way from standard QCT Monte Carlo trajectory methods, is related to a sum of ro-vibrational specific cross sections times a set of Einstein A values. As a test case we computed the CCS of single trajectories of CO. We investigated the sensitivity of the CCS to numerical convergence parameters and the dependence of the CCS on the

vibrational and rotational actions. We then applied the method to generating averaged CCS from O + CO collisions at 8 km/sec. The averaged CCS of these trajectories shows rich quantum-like structure including well-separated vibrational overtones and rotational band-heads, which becomes more pronounced with particular trajectory weighting methods.

The computation of average CCS is a straightforward extension of existing classical trajectory methods. Future work will apply the classical spectral methods developed here to collisions of polyatomic systems and analysis of polyatomic products. Using direct dynamics methods, which should yield forces and dipole moment functions at each trajectory point, it should be possible to calculate the average CCS straightforwardly, even for large molecular systems. With knowledge of the Einstein A coefficients of collision products, in principle it should be possible to deconvolve the average CCS and estimate probabilities to quantum specific final states. The hope is that the contributions from various vibrational modes will separate more cleanly in the classical spectra than in conventional QCT energy binning methods. Finally we note that the CCS should be directly comparable to the absorption spectrum of nascent collision products in molecular beam experiments, and so may provide a useful common point of comparison between theory and measurements.

For polyatomic systems, an important possible complication of the present analysis is that the products may undergo internal relaxation or some other process during the time period of the Fourier transform. Ergodic motion of the products may broaden the CCS to smooth over underlying structure, making the CCS difficult to interpret. We hope to explore all these issues in future work.

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FIGURE CAPTIONS

Figure 1. Classical collision spectra (CCS), $A_{\{u\}l}(\lambda)$, of CO computed with Eq. (6). Four spectra are shown, each with a different classical action *l*=(v,j): (v=0,j=90), (v=1,j=90),(v=2,j=90), and (v=3,j=90). (a) CCS over a large energy and intensity scale. The Δv notation suggests the corresponding quantum vibrational state transitions; (b) The same as (a) except the range of near Δv=0 transitions has been expanded; (c) The same as (a) excepts that the range of Δv=1 transitions has been expanded..

Figure 2. Classical collision spectra (CCS), $A_{\{u\}l}(\lambda)$, of CO computed with Eq. (6) over a limited spectral range, near Δv=1 transitions. Five spectra are shown, each with a different classical action *l*=(v,j): (v=0.5,j=90), (v=0.75,j=90),(v=1.0,j=90), (v=1.25,j=90), and (v=1.5,j=90).

Figure 3. The energy versus error in CCS peak position with respect to WKB transition energies for 11 different transitions associated with the progression, v,j=90 → v-1,j=89, where v = 1→11. CCS results are shown for 5 different choices of the semi-classical quantum numbers (n,r): (n=v-0.5,r=89.5), (n=v-0.5,r=90), (n=v-0.5,r=89), (n=v,r=89.5), and (n=v-1,r=89.5) with 'fine' integration parameters.

Figure 4. CCS Einstein A coefficients for fundamental (Δv=1, v→v-1,v=1-9,j=90→89) and overtone (Δv=2, v→v-2,v=2-8,j=90→89) progressions in CO as a function of the vibrational action. Results from three different CCS calculations are shown: (v,j=89.5 (F)) the rotational action r=89.5 with fine numerical convergence , (v,j=90.0 (F)) r=90.0 with fine numerical convergence, and (v=89.5 (S)) r=89.5 with standard numerical convergence. Einstein A values from Chandra *et al.*[14] are also plotted at the average vibrational action of the transition involved, (v-(v-1))/2 for the fundamental and (v-(v-2))/2 for the overtone.

Figure 5. CCS per energy for collisions of O + CO at 8 km/sec. Averaged CCS calculated from Eq. (7) with 'standard' integration parameters using a weight of one for each trajectory (CCS). Also shown are results from Eq. 9, "Reference" where the probabilities P_l are obtained from standard histogram binning into CO(v,j) states, the Einstein $A_{\{u\}l}$ are taken from Chandra *et al.*[14], and the peak positions are taken from the WKB energies of individual (v,j) lines.

Figure 6. The same as Figure 5 in the fundamental band transition region with various trajectory weights used for the averaged CCS: H denotes standard histogram binning, with a weight of 1.0 for each trajectory and only vibrational actions with v ≥ 0.5 are included, G(1/2) uses Gaussian weighting of trajectories centered on half integer vibrational actions starting with v=0, G(1) uses Gaussian weights

centered on integer vibrational actions starting at v=0.5. For the Reference spectrum only vibrational bins with v>0 are included.

Figure 7. The same as Figure 6, except in the overtone region.

Figure 8. The same as Figure 6, except in the second overtone region.

Figure 1

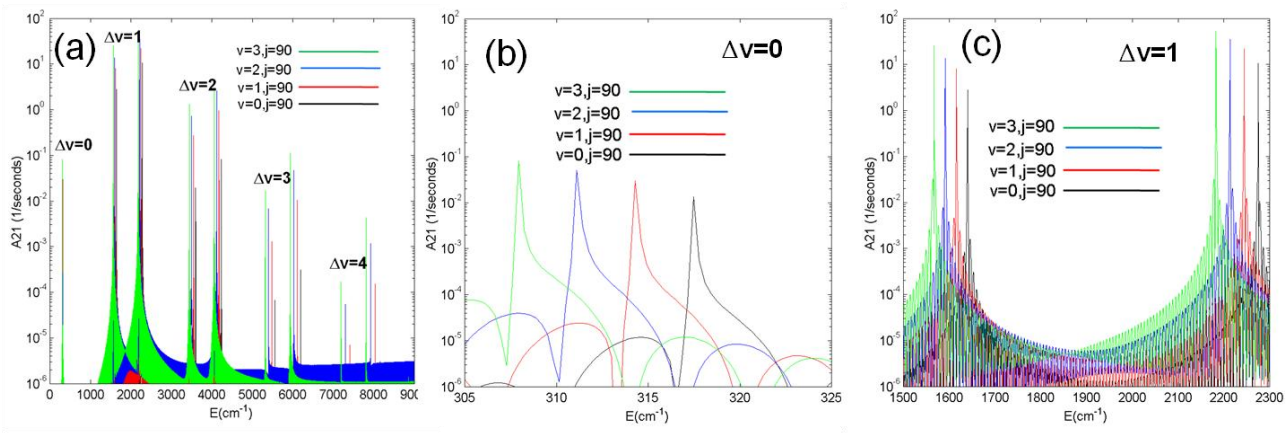


Figure 2

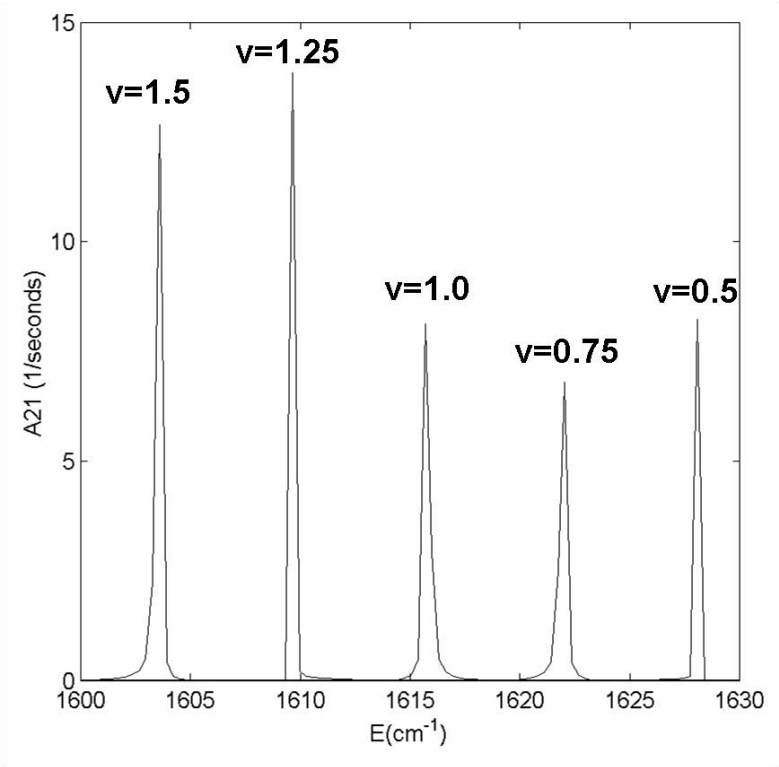


Figure 3

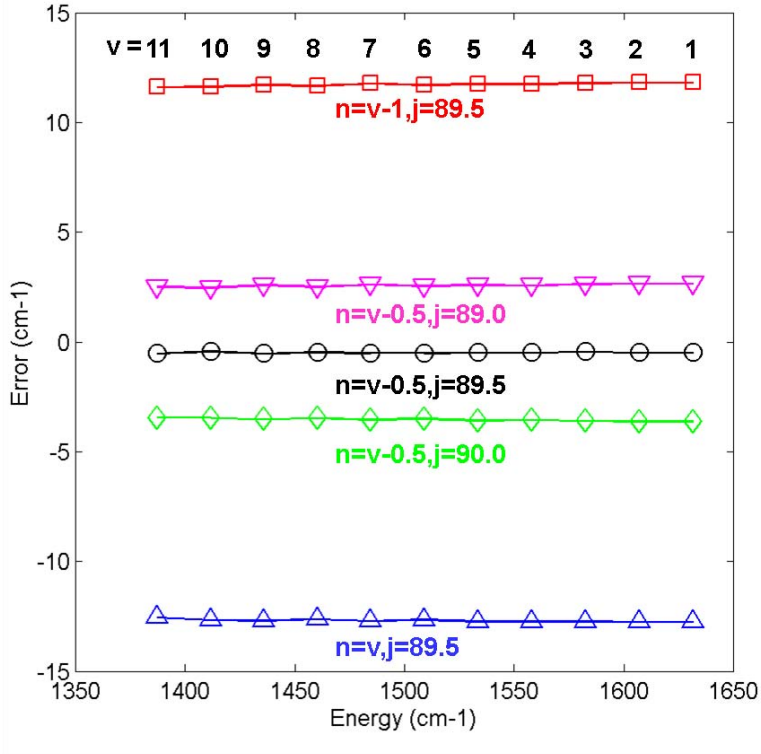

v = 11 10 9 8 7 6 5 4 3 2 1
n=v-1,j=89.5
n=v-0.5,j=89.0
n=v-0.5,j=89.5
n=v-0.5,j=90.0
n=v,j=89.5
Error (cm-1)
Energy (cm-1)
15
10
5
0
-5
-10
-15
1350
1400
1450
1500
1550
1600
1650

Figure 4

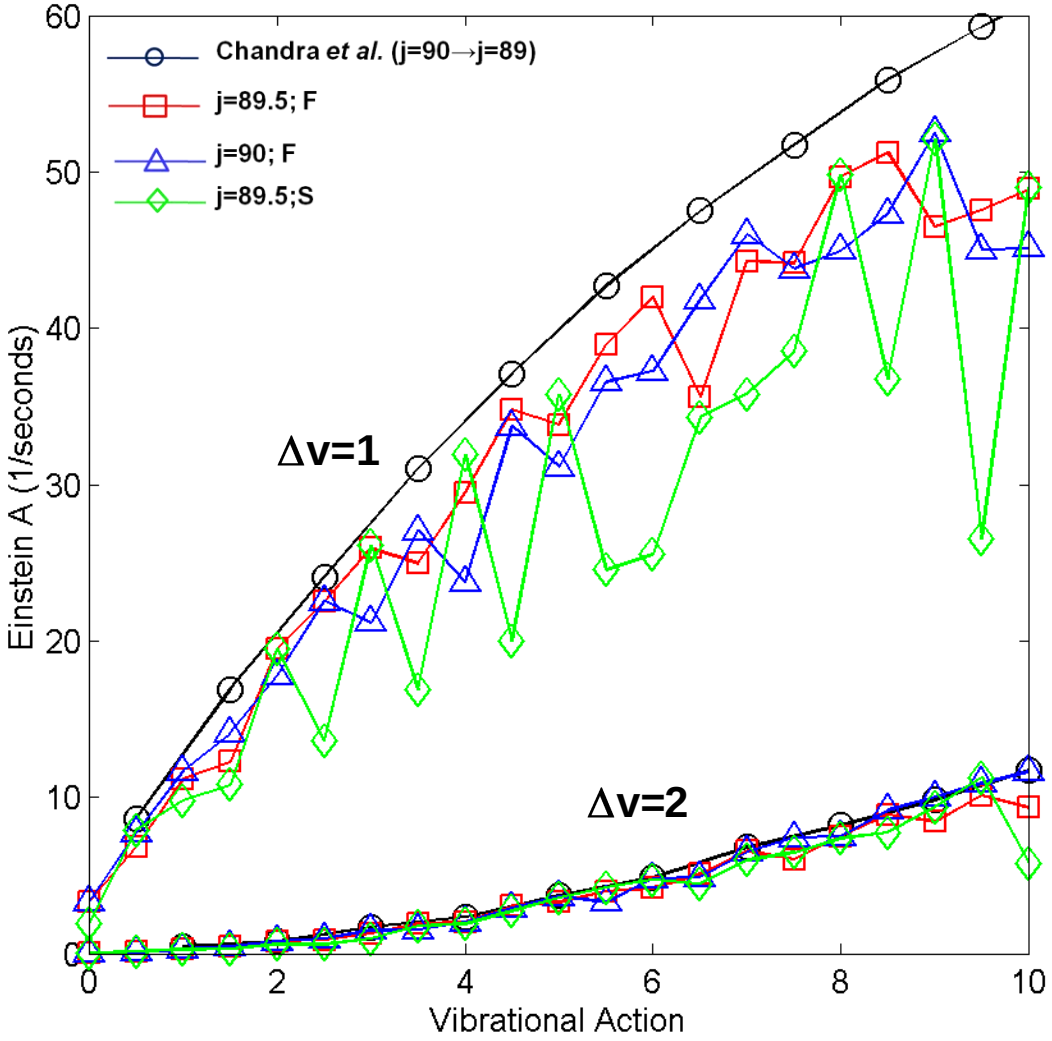

Chandra *et al.* (j=90→j=89)
j=89.5; F
j=90; F
j=89.5;S
Δv=1
Δv=2
Einstein A (1/seconds)
Vibrational Action
0
10
20
30
40
50
60
0
2
4
6
8
10

Figure 5

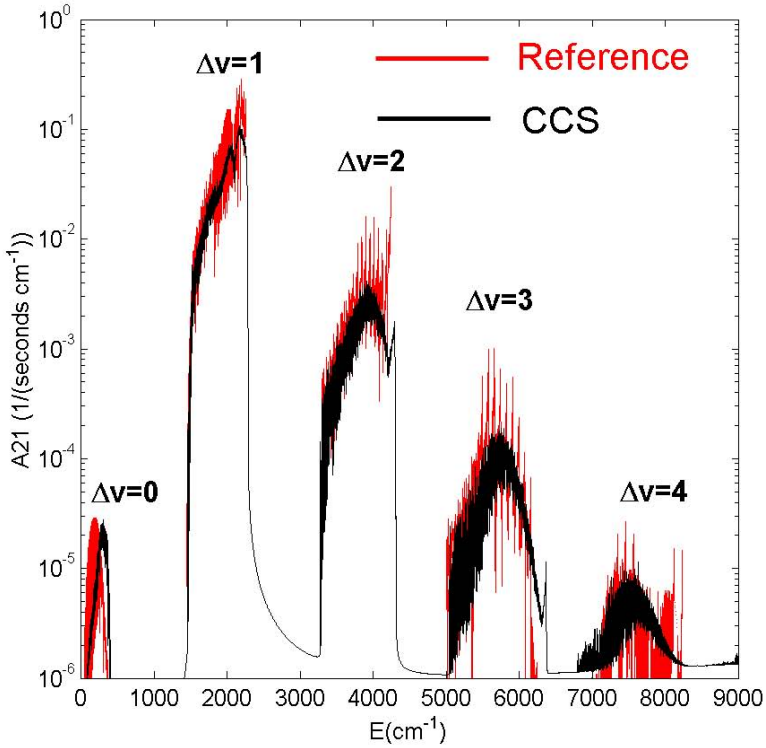

Reference
CCS
Δv=0
Δv=1
Δv=2
Δv=3
Δv=4
A21 (1/(seconds cm-1))
E(cm-1)
10^0
10^-1
10^-2
10^-3
10^-4
10^-5
10^-6
0
1000
2000
3000
4000
5000
6000
7000
8000
9000

Figure 6

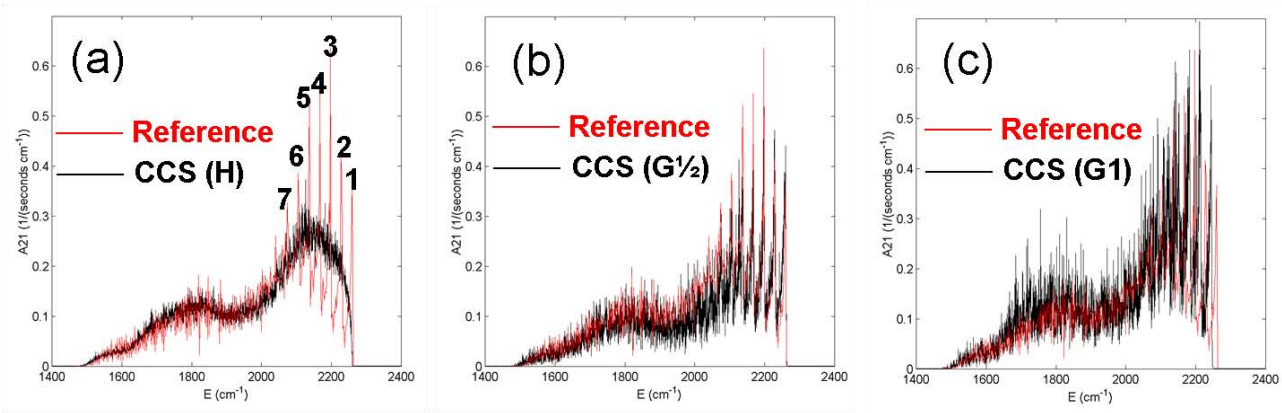


Figure 7

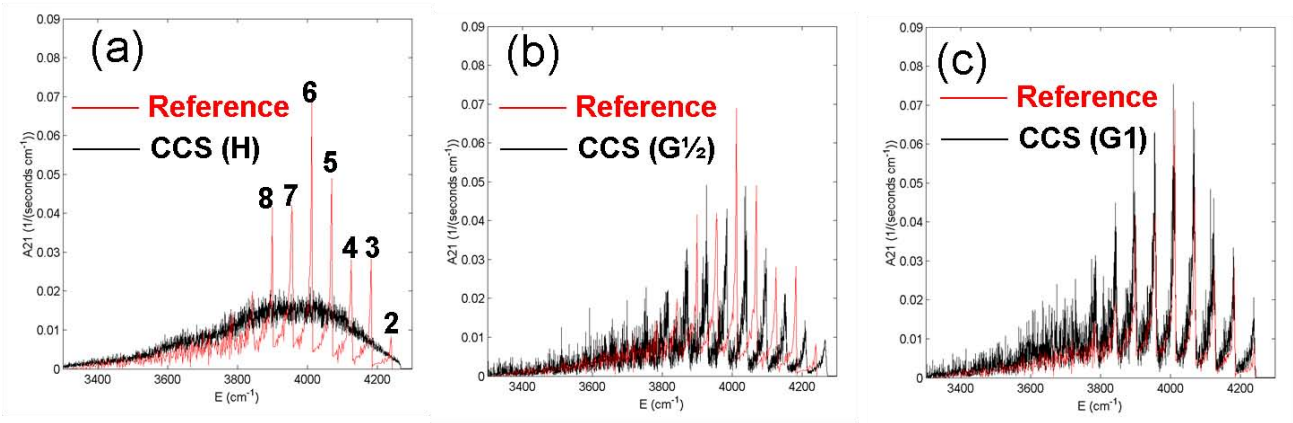
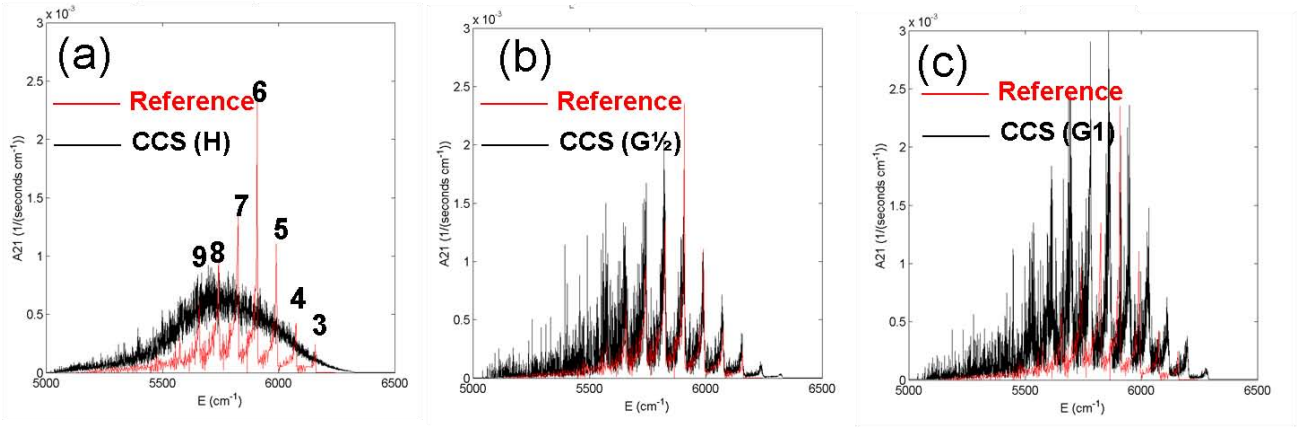


Figure 8


(a)
Reference
CCS (H)
6
7
5
9
8
4
3
(b)
Reference
CCS (G½)
(c)
Reference
CCS (G1)
A21 (1/(seconds cm-1))
E (cm-1)
x 10-3